Received: 2 March 2020 | Revised: 3 June 2020 | Accepted: 4 June 2020

DOI: 10.1002/jssc.202000239

JOURNAL OF SEPARATION SCIENCE

RESEARCH ARTICLE

Layered double hydroxide/poly(vinylpyrrolidone) coated solid phase microextraction Arrow for the determination of volatile organic compounds in water

Xinpei Li[1] | **Hangzhen Lan**[2,*] | **Dr. Kari Hartonen**[2] | **Matti Jussila**[2] | **Xinghua Wang**[3] | **Marja-Liisa Riekkola**[2]

[1] School of Molecular Science and Engineering, South China University of Technology, Guangzhou 510640, P. R. China

[2] Department of Chemistry and Institute for Atmospheric and Earth System Research, P.O. Box 55, FI-00014 University of Helsinki, Helsinki, Finland

[3] College of Chemistry, Jilin University, Qianjin Street 2699, Changchun 130012, P. R. China

Correspondence
Dr. Kari Hartonen, Department of Chemistry and Institute for Atmospheric and Earth System Research, P.O. Box 55, FI-00014 University of Helsinki, Helsinki, Finland.
Email: kari.hartonen@helsinki.fi.

*Current address: Hangzhen Lan, Department of Food Science and Engineering, College of Food and Pharmaceutical Sciences, Ningbo University, Ningbo, 315832, P. R. China.
Email: lanhangzhen@nbu.edu.cn

Funding information
China Scholarship Council, Grant/Award Numbers: 201706170136, 201508330310; Academy of Finland, Grant/Award Number: grant no. 307331

Today, wide variety of adsorbents have been developed for sample pretreatment to concentrate and separate harmful substances. However, only a few solid phase microextraction Arrow adsorbents are commercially available. In this study, we developed a new solid phase microextraction Arrow coating, in which nanosheets layered double hydroxides and poly(vinylpyrrolidone) were utilized as the extraction phase and poly(vinyl chloride) as the adhesive. This new coating entailed higher extraction capacity for several volatile organic compounds (allyl methyl sulfide, methyl propyl sulfide, 3-pentanone, 2-butanone, and methyl isobutyl ketone) compared to the commercial Carboxen 1000/polydimethylsiloxane coating. Fabrication parameters for the coating were optimized and extraction and desorption conditions were investigated. The validation of the new solid phase microextraction Arrow coating was accomplished using water sample spiked with volatile organic compounds. Under the optimal conditions, the limits of quantification for the five volatile organic compounds by the new solid phase microextraction Arrow coating and developed gas chromatography with mass spectrometry method were in the range of 0.2-4.6 ng/mL. The proposed method was briefly applied for enrichment of volatile organic compounds in sludge.

KEYWORDS
gas chromatography, layered double hydroxides, poly(vinylpyrrolidone), solid phase microextraction Arrow, volatile organic compounds

1 | INTRODUCTION

Sewage Treatment Plants (STPs) produce large amounts of sewage, which are the major sources of malodors. Normally, volatile sulfur compounds (VSCs) are accepted to be the cause of nuisance emissions. While VSCs alone inadequately represent the odour impacts of the emissions,

Article Related Abbreviations: HS, headspace; LDH, layered double hydroxide; ND, not detected; NLDH, nanosheet layered double hydroxide; PAH, polyaromatic hydrocarbon; PVC, poly(vinyl chloride); PVP, poly(vinylpyrrolidone); STP, sewage treatment plant; TGA, thermogravimetric analysis; THF, tetrahydrofuran; TIC, total ion chromatogram; VOC, volatile organic compound; VSC, volatile sulfur compound

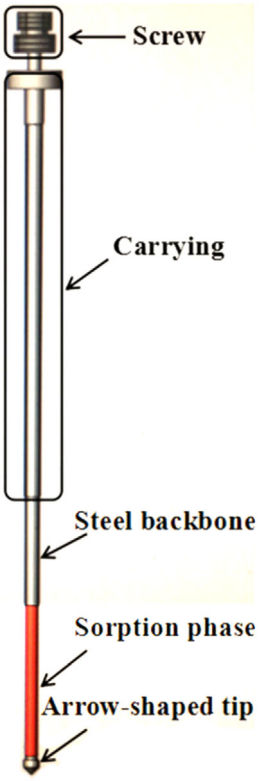

FIGURE 1 Detailed view of the SPME Arrow

volatile organic compounds (VOCs) not containing sulfur element also have contributions to the overall sensorial properties of emissions [1]. Most of the VOCs in the malodors have deleterious impacts on citizens living near the STPs owing to their high toxicity, mutagenicity, and carcinogenicity [2]. Therefore, VOCs emitted from the sewage or other wastes should be monitored in order to ensure that humans are more clearly aware of their living environment and impel regulators to establish reliable, strict, accurate, and powerful environmental protection standards.

Solid phase microextraction (SPME) technique is highly recommended to extract and preconcentrate VOCs at trace levels from complex matrices [3, 4]. The free-solvent characteristic of SPME technique has made it as the predominant microextraction technique in analytical chemistry today [5, 6]. However, SPME fiber also has some drawbacks such as small sorption phase volume [7, 8], the fiber fragility, stripping of the coating, and bending of the needle [6]. Recently, SPME Arrow has been specifically developed to overcome these problems. The detailed structure of SPME Arrow (Fig. 1) includes a stainless-steel backbone, the carrying, the screw, the enlarged sorption phase, and an Arrow-shaped tip. The carrying prevents the physical damage of the sorption phase during transfer and the Arrow tip enable the gentle penetrations into the sample vial or GC inlet septum. According to the previous reports, SPME Arrow technique has been applied for the measuring of VOCs in wastewater, atmospheric air, and food samples [9-12]. As we know, the design and preparation of the SPME Arrow coating material are of particular importance in the whole extraction and separation process. Thus, alternative materials to commercials ones are needed.

A class of anionic clays known as layered double hydroxides (LDHs), which are composed of octahedral brucite-like layers and interlayer water molecules, has attracted substantial attention from both industry and academia [13]. To our knowledge, LDHs have become popular as catalysts, catalyst supports, adsorbents, drug exchangers, sensory and electric materials [14]. Based on the properties of the permanent positive charged layers, high porosity, high anion-exchange capacity, large surface area, good thermal stability, and water-resistant structure [15], the reported studies have focused on the modification of LDHs for the determination of trace and ultra-trace amount of inorganic anions [16]. So far, LDHs have been applied in the adsorption of naphthols [17], phenols [18], polyaromatic hydrocarbons (PAHs) [19], chlorinated organic compounds [20], aromatic acids [21], dyes [22]. In the aspect of the LDHs synthesis, the Mg/Al LDHs are facilely prepared by means of simple low-cost coprecipitation method [23]. The layers of the synthesized Mg/Al LDHs are connected tightly by electrostatic interactions and hydrogen bonds between LDHs layers and contents of the gallery. The formed rigid networks cannot facilitate the anions or molecules accessing to the interlayers of pristine LDHs [24], resulting in the relatively weak adsorption for the analytes. The exfoliation of LDHs leads to surface layers to be accessible for chemical reactivity, and the exfoliated products nanosheet-LDHs (NLDHs) can form hydrogen bonds with the analytes due to abundant hydroxyl groups. In addition, the enhanced mechanical strength and reduced flammability [25] of NLDHs ensure its applicability as the coating material of the SPME Arrow.

The applications of poly(vinylpyrrolidone) (PVP) to remove phenolic compounds from fruit juices and plant extracts are well documented [26, 27]. Due to the presence of hydrogen bonds between the imide group in PVP and the hydroxyl group or sulfhydryl group in the analytes [28], PVP will be favorable for the adsorption of ketones and sulfur VOCs.

In this study, we investigated whether the integration of the LDH nanosheets and the PVP will be effective as the SPME Arrow coating. In the new coating, poly(vinyl chloride) (PVC) was served as the adhesive. As we all know, sample preparation technique based on headspace SPME (HS-SPME) coupled with GC-MS has been widely used in the analysis of VOCs in various status samples (gaseous, liquid, and solid) [24, 26, 29]. Thus, GC-MS was employed to analyze the target compounds.

2 | MATERIAL AND METHODS

2.1 | Instruments and reagents

The analytical standards (allyl methyl sulfide, methyl propyl sulfide, 3-pentanone, 2-butanone, and methyl isobutyl ketone) were chosen and supplied by Sigma-Aldrich (St. Louis, USA). Magnesium nitrate hexahydrate ($Mg(NO_3)_2$•$6H_2O$) was purchased from E. Merck (Darmstadt, Germany). Aluminium nitrate ($Al(NO_3)_3$•$9H_2O$) was from BDH Chemicals (Poole, England). Sodium hydroxide (0.1 M, NaOH) and hydrochloric acid (0.1 M, HCl) were from Oy FF-Chemicals Ab (Haukipudas, Finland). Sodium carbonate (Na_2CO_3), PVP, PVC, tetrahydrofuran (THF) (≥99.9%), acetone, and methanol (≥99.9%) were from Sigma-Aldrich (St. Louis, USA). Ultrapure water (Millipore DirectQ-UV, Billerica, MA, USA) was used for the preparation of stock standard and sample solutions.

Uncoated SPME Arrows (coating length 20 mm) and Carboxen 1000/polydimethylsiloxane coated SPME Arrows (Carboxen 1000/PDMS, sorbent film thickness 120 μm, coating length 20 mm) were supplied by BGB Analytik (Zurich, Switzerland) and CTC Analytics (Zwingen, Switzerland), respectively. The SenTix 42 pH-electrode was obtained from Wissenschaftlich-Technische Werkstätten (Germany).

The surface morphology of the SPME Arrow coated with NLDHs/PVC/PVP was studied by SEM (Hitachi, model S-4800, Japan). In addition, FTIR spectra of coating material were measured with Spectrum one spectrometer (Perkin Elmer, Waltham, MA, USA) in the region of from 400 to 4000 cm^{-1}. Thermogravimetric analysis (TGA) was conducted with a Mettler Toledo Stare system under nitrogen flow. The TGA heating program was from room temperature up to 700°C at a rate of 10°C/min.

2.2 | Coprecipitation synthesis of Mg-Al layered double hydroxides

Aqueous solution (20 mL) of 1.875 M $Mg(NO_3)_2$•$6H_2O$ and 0.625 M $Al(NO_3)_3$•$9H_2O$ was added drop-wise into 50 mL of 0.5 M Na_2CO_3 aqueous solution. The pH value was kept at ca. 9.0 by dropping 4.0 M NaOH. The solution was stirred at room temperature for 30 min. The obtained LDH wet cake was dried in oven at 95°C, then the LDH solids were transferred into the 200 mL of boiling water in order to be exfoliated under the magnetic stirring. The exfoliation process was stopped until water was completely vaporized. In the end, the pristine LDHs turned into thinner LDHs with a few layers not the monolayered double hydroxides. The final products were grounded with mortar and pestle, and then sealed in the vial at room temperature.

2.3 | Preparation of nanosheet layered double hydroxides/poly(vinyl chloride)/poly(vinylpyrrolidone) solid phase microextraction Arrow coating

Aqueous PVP solution was prepared by adding 400 mg PVP into 10 mL ultrapure water, followed by slow addition of 10 mL acetone. The speed of acetone addition should be slow to avoid formation of cloudy suspension.

The PVC concentration in THF influenced to the viscosity of the mixture, and further to the robustness of SPME Arrow coating. In addition, the PVC concentration also played an important role in the surface morphology of SPME Arrow coating. The stock PVC/THF solutions were prepared by adding different amounts of PVC into 20 mL THF.

The thickness of NLDHs/PVC/PVP SPME Arrow coating was primarily determined by the SPME Arrow dipping times in NLDHs/PVC suspensions. The NLDHs/PVC suspensions were constructed by mixing adequate masses of NLDHs and 1 mL PVC/THF solution in 1 mL centrifuge tube. Subsequently, the suspensions were agitated by vortex stirrer to form even mixtures.

Uncoated SPME Arrow was successively washed in 10 mL methanol and 10 mL of 0.1 M NaOH under 15 min sonication. Then, the SPME Arrow was rinsed with ultrapure water (three times) and immersed into 10 mL of 0.1 M HCl for 1 h to be etched. At last, the SPME Arrow was washed three times with ultrapure water and dried at room temperature. The bare SPME Arrow steel was firstly immersed into the NLDHs/PVC solutions for 3 s and then slowly pulled out the solution. After the SPME Arrow coating was dried, the above-mentioned process was repeated five times for it. Then the coated SPME Arrow was heated for 10 min in an oven at 95°C to remove THF and to obtain robust coating. The robust SPME Arrow was dipped two times in the PVP solution (dipping was followed by drying process in an oven before next dipping). Finally, the NLDHs/PVC/PVP SPME Arrow was inserted into the GC-MS injector port, where the temperature was set to 230°C. This aging step aimed to remove the contaminants (volatile organic solvents and unstable molecules) and form the robust and specific coating.

2.4 | Preparation of standard solution and sample collection

Primary individual solutions of allyl methyl sulfide, methyl propyl sulfide, 3-pentanone, 2-butanone, and methyl isobutyl ketone were prepared in ultrapure water at a concentration of 1000 μg/mL and stored at 4°C in the dark. Working standard solutions were prepared on a daily basis

by further mixing the primary individual solutions and diluting with ultrapure water. Solid sludge particles were collected from wastewater samples by filtering. Then the sludge was dried (48 h, 45°C) and homogenized [30]. The obtained sludge samples were stored in the refrigerator at 4°C.

2.5 | Solid phase microextraction Arrow procedures

Ultrapure water (2 mL) spiked with five VOCs standards was added into a HS vial (20 mL) containing stirring bar (10 × 3 mm). SPME Arrow was inserted into the HS of the vial. After a certain extraction time, the SPME Arrow was heated to release VOCs in the injector port. The VOCs were delivered into a GC capillary column for separation and then transferred into MS for ionization, m/z separation, and detection of the ions.

2.6 | Chromatographic conditions

Samples were analyzed with an Agilent 6890 gas chromatograph equipped with an Agilent 5973 N mass selective detector (Agilent Technologies, Palo Alto, USA). An Inert-Cap for amines analytical column (30 m × 0.25 mm (i.d.), GL Sciences, Tokyo, Japan) was connected to a deactivated fused silica retention gap (1.5 m × 0.53 mm (i.d.), Agilent Technologies). The column oven temperature program was as follows: 40°C held for 1 min and ramped at a rate of 35°C min^{-1} to 250°C, where the temperature remained for 5 min.

Helium (99.996%, AGA, Espoo, Finland) was used as carrier gas in a constant flow rate mode (1 mL/min). The SPME Arrow was inserted through a standard inlet septum into a split/splitless inlet liner (internal diameter, 2.0 mm) and the desorption procedure was executed in splitless mode. The injector temperature was 210°C. The GC-MS transfer line, the ion source, and quadrupole temperatures were at 260, 200, and 150°C, respectively. Electron ionization 70 eV was used and total ion chromatogram (TIC) was obtained in the scan range of m/z = 30-300.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of the prepared solid phase microextraction Arrows

The surface morphologies of PVC, PVP, NLDHs/PVC, and NLDHs/PVC/PVP SPME Arrows were characterized by SEM (Fig. 2). It was apparently observed that the surfaces of PVC and PVP SPME Arrow coatings were smooth (Fig. 2E and F) but NLDHs/PVC/PVP and NLDHs/PVC SPME Arrow coatings were rough (Fig. 2A and C). In addition, the surface of NLDHs/PVC/PVP SPME Arrow was smoother than that of NLDHs/PVC SPME Arrow (Fig. 2B and D), which is due to the cover of PVP.

The FTIR spectra of the PVC, PVP, and NLDHs/PVC/PVP materials were recorded. Two characteristic absorption bands at 1788 and 832 cm^{-1} were found on the spectrum of the pure PVP (Supporting information Fig. S1B), which appear in the spectrum of NLDHs/PVC/PVP hybrids (Supporting information Fig. S1C) at 1788 and 834 cm^{-1}. The adsorption bands at 609 and 690 cm^{-1} from the curve A are ascribed to the C-Cl stretching vibration of PVC, and the corresponding bands at 606 and 684 cm^{-1} were observed on the curve C.

The TGA measurement was employed to inspect the thermal stability of the NLDHs/PVC/PVP coating. From Supporting information Fig. S2, it can be observed that the quality was slowly reduced from room temperature to 150°C. The cause of slow reduction is the loss of crystalline water in the NLDHs. From 150 to 250°C, the curve is declined with the similar and small slope values, which indicates that the NLDHs/PVC/PVP coating is thermostable at this range.

3.2 | Optimization of nanosheet layered double hydroxides/poly(vinyl chloride)/poly(vinylpyrrolidone) coating preparation procedures

To obtain efficient extraction performance, some important experimental factors, including mass of PVC in THF, amount of NLDHs in 1 mL PVC/THF solution, dipping times in NLDHs/PVC/THF solutions, dipping times in the PVP aqueous solution, condition time and temperature of NLDHs/PVC/PVP coating, extraction and desorption time and desorption temperature, were investigated and optimized. The variables were tested using ultrapure water containing 0.5 μg/mL of the selected VOCs. All experiments were performed in triplicate by varying one factor while keeping others constant at their preoptimized values. This work assumed that there were no interactions between different experimental factors. The extraction performance of NLDHs/PVC/PVP SPME Arrow was represented by the relative average recovery for each optimization condition.

In 20 mL THF, different PVC masses (100, 250, 400, 500, 700 mg) were first investigated. With 100 mg PVC, the prepared coating was too loose and easily detached to be used repeatedly (data not shown). With higher PVC

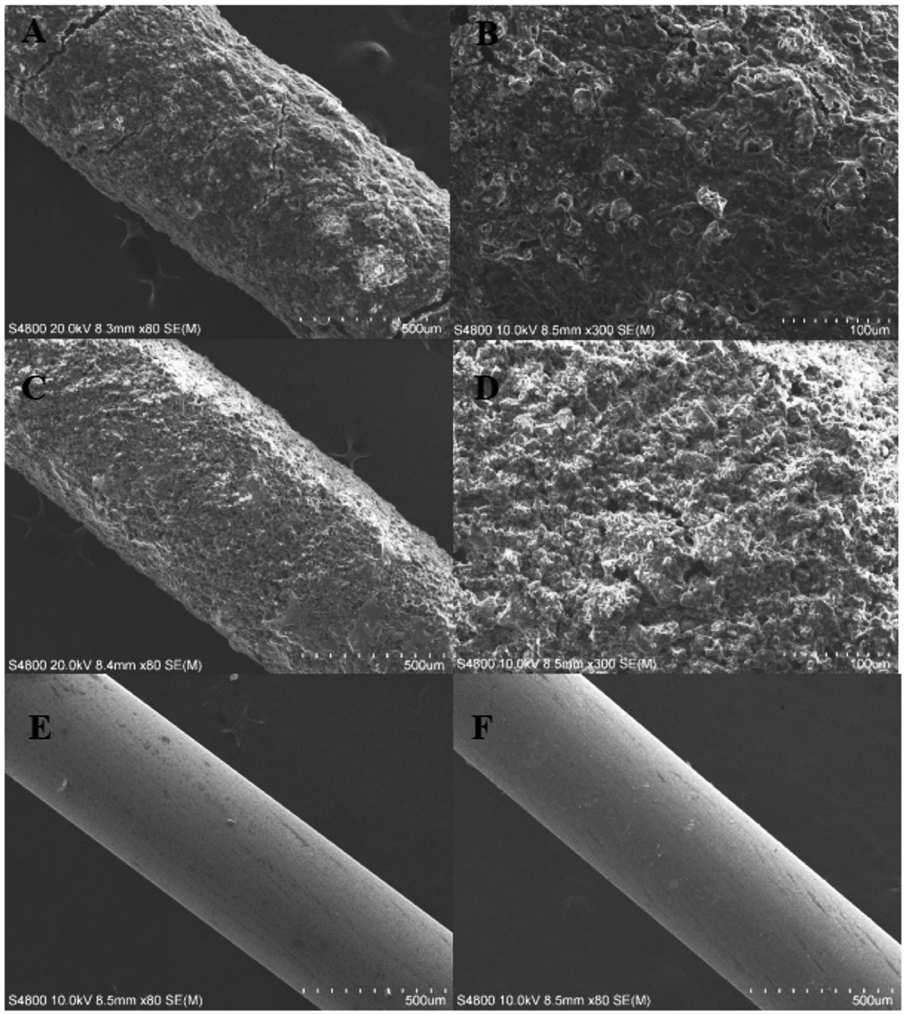

FIGURE 2 SEM images of the surface of SPME Arrow coatings: the overall morphology of NLDHs/PVC/PVP SPME Arrow (A); the amplified images of NLDHs/PVC/PVP SPME Arrow (B); the overall morphology of NLDHs/PVC SPME Arrow (C); the amplified images of NLDHs/PVC SPME Arrow (D); the overall morphology of PVP (E); and PVC (F) SPME Arrows

mass, the coating robustness was increased. However, with one-by-one dipping operation, it is difficult to fabricate a relatively smooth and identical thick coating. The lower part of SPME Arrow rod was always much thicker than the upper part. When the upper part had a certain thickness, the lower part was too thick to enclose the coating by pushing down the carrying. Increasing the amount of PVC from 200 to 500 mg in the THF solution facilitated the good extraction efficiency of the SPME Arrow, while it was decreased afterwards (Supporting information Fig. S3A). This decrease may be caused by the thicker PVC, which obstructs the diffusion of analytes into the coating. Thus, the PVC mass was set to 400 mg.

The increase of NLDHs masses (from 200 to 400 mg) in PVC solutions improved the extraction efficiency of the SPME Arrow (Supporting information Fig. S3B). With more than 400 mg of NLDHs, it was difficult to obtain uniform coating. Thus, 400 mg was selected for this parameter to compromise between the extraction efficiency and the coating uniformity.

The dipping times in NLDHs/PVC suspensions influenced the coating thickness and the extraction capacity of the coating. The extraction recoveries of analytes were significantly increased with the number of dipping increasing from two to five, and then remained stable with the dipping times further increasing to six (Supporting information Fig. S3C). However, dipping more than six times led to smashing of the coating during closing the carrying of the SPME Arrow. Hence, five times for the dipping was selected as optimum.

The extraction capacity of the coating was also related to the content of PVP (Supporting information Fig. S3D). The extraction performance of the coating without PVP was undesirable (data not shown). The extraction recoveries when dipping two times in PVP solution reached to the highest level. Dipping more than three times the SPME

Arrow into the PVP solution limited the diffusion of analytes into the inside coating and thereby decreased the extraction recoveries.

The influence of condition temperature (210, 230, and 240°C) was investigated by adjusting the injector port temperature (Supporting information Fig. S4A). The extraction recoveries of analytes obviously increased with the condition temperature increasing from 210 to 230°C and remained stable with the further increase. To ensure the repeatability of the experimental data and obtain the efficient extraction performances, 230°C was chosen as the most suitable condition temperature.

The effect of condition time of NLDHs/PVC/PVP SPME Arrow on the extraction performance was studied by exposing SPME Arrow into the GC-MS injector port for a certain period of time (1, 3, 5, 7, 10, 12, 24, and 48 h). With the increase in condition time, the SPME Arrow efficiency enhanced until the condition time reached 12 h (Supporting information Fig. S4B). With the longer condition times, no changes in the results were observed. Therefore, the condition time of NLDHs/PVC/PVP SPME Arrow was set to 12 h.

3.3 | Optimization of headspace solid phase microextraction Arrow procedures

Given the spillage of water under stirring, the suitable volumes (1, 2, and 3 mL) of water were evaluated. With the water volumes increasing from 2 to 3 mL, the extraction efficiencies of the analytes had no obvious variations (data not shown).

As SPME is an equilibrium-based extraction method, extraction time has a direct impact on the amounts of extracted analytes on the extraction phase and the repeatability of the method. Therefore, the effects of extraction time were investigated in the range of 5-30 min (Supporting information Fig. S5A). The extraction equilibrium was reached at 25 min for all the analytes.

The desorption temperature was investigated in the range of 200-240°C (Supporting information Fig. S5B). High injection temperature promotes the desorption of compounds from the SPME Arrow to the GC inlet and reduces the desorption time, while high temperature can also cut the lifespan of the SPME Arrow coating. To the end, 210°C was set as the optimal desorption temperature.

Long desorption time generally improves the sensitivity of the method [31]. However, in our preoptimization test, the desorption time longer than 1 min had no obvious influence on the experimental result. Thus, desorption times less than 1 min (6, 15, 30, 45, and 60 s) were tested (Supporting information Fig. S5C). The extraction recoveries significantly increased with desorption time increasing from 6 to 15 s, which indicates that the thorough release of the analytes was achieved in 15 s.

3.4 | Comparison of self-made and commercial solid phase microextraction Arrows

The PVC, PVP, NLDHs/PVC, and NLDHs/PVC/PVP coatings were individually prepared to extract 0.5 μg/mL analytes under the optimized conditions. Both PVP and PVC SPME Arrows exhibited unsatisfactory extraction abilities for these five standards. In addition, low thermal stability and short service time limited their application. When SPME Arrow was coated with NLDHs/PVC, the coating was too wet and swelled to stick to the SPME Arrow. Thus, NLDHs/PVC/PVP coated SPME Arrow was selected for the further study.

Three conventional SPME Arrows (PDMS, Carboxen WR/PDMS, and Carboxen 1000/PDMS SPME Arrows) were selected to embody the extraction efficiencies based on the proposed SPME Arrow. The extraction efficiencies of conventional SPME Arrows were tested by extracting the five standards under the same conditions with the proposed method. Preliminary trials (data not shown) indicated that the best commercial sorbent for extracting these five VOCs was Carboxen 1000/PDMS. Finally, Carboxen 1000/PDMS SPME Arrow was used for further comparison with the NLDHs/PVC/PVP coated SPME Arrow. As can be seen from Fig. 3, the peak area signals of analytes by NLDHs/PVC/PVP SPME Arrow were higher than those by the commercial SPME Arrow. The high adsorption capacity of the new coating for VOCs containing oxygen and sulfur atoms is due to the components of the nanosheet-LDHs and PVP. The NLDHs expose much more hydroxyl groups than those of pristine LDHs, due to the calcination and exfoliation processes. In addition, PVP is composed of carbonyl groups. Furthermore, the oxygen-containing functional groups facilitate the polarity of the new coating, promoting the adsorption of the five polar VOCs through the formation of hydrogen bonds. Additionally, the extra *p*-electrons of pyrrolic nitrogen of PVP can improve active sites on the new coating surface to enhance the adsorption performances [32].

3.5 | Method validation

Under the optimal extraction conditions, NLDHs/PVC/PVP SPME Arrow-GC-MS method performance was investigated for the linear range, the LOQs, and precision. LOQs were calculated according to the 10 times signal-to-noise (S/N).

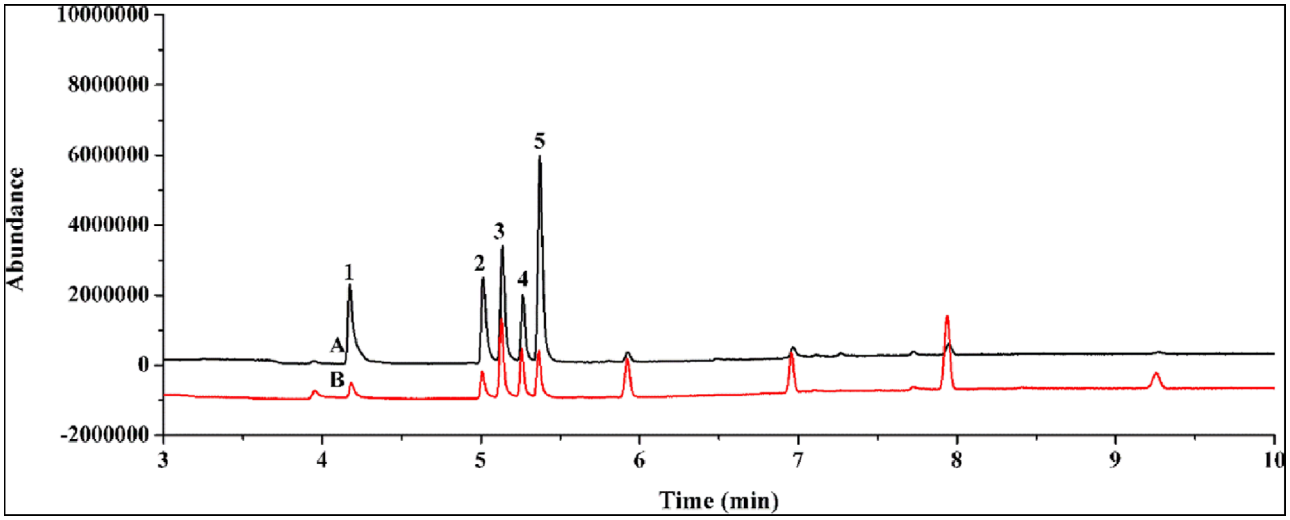

FIGURE 3 Chromatograms of the five VOCs (1, 2-butanone; 2, 3-pentanone; 3, allyl methyl sulfide; 4, methyl propyl sulfide; 5, methyl isobutyl ketone) in ultrapure water extracted by NLDHs/PVC/PVP SPME Arrow (A) and commercial carboxen 1000/PDMS SPME Arrow (B)

TABLE 1 Analytical features of NLDHs/PVC/PVP coated SPME Arrow and GC-MS for the determination of the VOCs

					One Arrow (n = 5) (%)					
					Interday		Intraday		Arrow-to-Arrow (*n* = 3) (%)	
Analytes	Linear range (μg/ mL)	R^2	LOD (ng/ mL)	LOQ (ng/mL)	Recoveries	RSD	Recoveries	RSD	Recoveries	RSD
2-Butanone	0.005-0.8	0.9994	1.4	4.6	96.1	4.5	92.5	7.2	97.5	7.7
3-Pentanone	0.005-1	0.9953	1.2	3.9	96.9	5.4	94.8	6.2	89.3	12.3
Allyl methyl sulfide	0.005-1	0.9984	1.1	3.6	95.2	4.5	97.6	8.6	100.9	9.1
Methyl propyl sulfide	0.005-1	0.9980	0.7	2.2	89.0	4.6	93.9	9.8	93.5	11.3
Methyl isobutyl ketone	0.001-1	0.9970	0.06	0.2	102.5	11.4	96.4	6.7	94.3	10.1

Linear ranges, determination coefficients, and LOQs are listed in Table 1. For 3-pentanone, allyl methyl sulfide, and methyl propyl sulfide (concentration in the range of 0.005-1 μg/mL), the peak areas were linear with the determination coefficients in the range of 0.9953-0.9984. The peak areas were linear with the concentration of 0.001-1 and 0.005-0.8 μg/mL for methyl isobutyl ketone and 2-butanone with the determination coefficients in the range of 0.9970-0.9994, respectively. The LOQs of the five VOCs ranged from 0.2 to 4.6 ng/mL.

The precision and accuracy were presented by RSDs. The precisions (Table 2) were obtained by repeating five times the extraction of the VOCs in ultrapure water at the concentration of 0.005, 0.01, 0.25, and 0.5 μg/mL. The RSDs were between 2.7 and 16.6% with the extraction recoveries of 72.8-113%. The intra- and interday precisions were determined by analyzing the samples five times in one day and once a day in five consecutive days, respectively. The RSDs were in the range of 4.5-11.4% (Table 1). The SPME Arrow-to-SPME Arrow reproducibility was obtained by using three different SPME Arrows prepared under the same coating process. The obtained RSDs were less than 12.3% (Table 1).

3.6 | Method applicability to sludge samples

Preliminary investigation was conducted to check if the self-made SPME Arrow could enrich VOCs from the sludge sealed in the vial. Using HS sampling, 2-butanone, and methyl isobutyl ketone are clearly observed on the chromatogram (Supporting information Fig. S6). The concentrations of 2-butanone and methyl isobutyl ketone were semiquantified by assuming the same extraction conditions of waste sludge samples with those of spiked ultrapure water, since HS sampling was utilized in both. In line with the calibration curve, the concentrations of 2-butanone and methyl isobutyl ketone were roughly calculated as 50.7 and 47.7 ng/g, respectively (Table 3). The

TABLE 2 Analytical results of NLDHs/PVC/PVP coated SPME Arrow and GC-MS for the determination of the VOCs in ultrapure water spiked with the four concentration level VOCs standards

Analytes	0.005 μg/mL		0.01 μg/mL		0.25 μg/mL		0.5 μg/mL	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
2-Butanone	83.4	12.3	89.4	9.3	92.6	15.4	95.9	2.7
3-Pentanone	72.8	12.3	76.9	11.3	83.8	7.1	96.4	3.5
Allyl methyl sulfide	102	9.1	107	8.8	91.8	10.0	89.7	6.6
Methyl propyl sulfide	80.4	8.0	113	8.4	88.9	12.4	97.1	8.9
Methyl isobutyl ketone	96.4	16.6	78.4	10.6	99.9	4.6	95.0	9.9

TABLE 3 Analytical results obtained with NLDHs/PVC/PVP coated SPME Arrow and GC-MS for the VOCs in sludge without spiking

Analytes	Sludge (ng/g)
2-Butanone	50.7
3-Pentanone	ND
Allyl methyl sulfide	ND
Methyl propyl sulfide	ND
Methyl isobutyl ketone	47.7

ND, not detected.

method looks promising for the sludge sample. Further research will be needed to modify the coating further, aiming to remove the interferences, and to construct quantitative method of VOCs from the complicated matrix.

4 | CONCLUSIONS

The competitive features of nanosheet LDHs and PVP were integrated, and the performance of SPME Arrow coated with NLDHs/PVC/PVP was studied. The new coating efficiently enriched the chosen analytes as expected. The extraction efficiencies for the selected VOCs with the developed SPME Arrow were much higher compared to the commercial SPME Arrows (PDMS, Carboxen WR/PDMS, and Carboxen 1000/PDMS SPME Arrows). The mechanical property of SPME Arrow coating satisfied the operation requirement. However, one issue is that the SPME Arrow coating was considerably hydrophilic, causing the inferiorities (easily being wet and swelled) in the aqueous phase. The novel SPME Arrow also efficiently adsorbed many other VOCs with recoveries slightly less than or equal to those extracted by commercial SPME Arrows.

ACKNOWLEDGEMENTS

Financial support was provided by China Scholarship Council (X.L. Grant no. 201706170136, H.L. Grant no. 201508330310), and the Finnish Centre of Excellence in Atmospheric Science—From Molecular and Biological Processes to the Global Climate (Grant no. 307331).

CONFLICT OF INTEREST

The authors have declared no conflict of interest.

ORCID

Dr. Kari Hartonen https://orcid.org/0000-0003-4821-2355

REFERENCES

1. Kotowska, U., Zalikowski, M., Isidorov, V. A., HS-SPME/GC-MS analysis of volatile and semi-volatile organic compounds emitted from municipal sewage sludge. Environ. Monit. Assess. 2012, 184, 2893–2907.
2. Costa, M., Baldasano, J. M., Development of a source emission model for atmospheric pollutants in the Barcelona area. Atmos. Environ. 1996, 30, 309–318.
3. Razmi, H., Khoshmanesh, S. M., An in situ electrochemical fabrication of layer by layer graphenized graphite polyaniline as a stable solid-phase microextraction fiber coating for trace environmental analysis. J. Sep. Sci. 2019, 42, 1364–1373.
4. Liang, D. P., Liu, W. J., Raza, R., Bai, Y., Liu, H. W., Applications of solid-phase micro-extraction with mass spectrometry in pesticide analysis. J. Sep. Sci. 2019, 42, 330–341.
5. Aulakh, J. S., Malik, A. K., Kaur, V., Schmitt-Kopplin, P., A review on solid phase micro extraction–high performance liquid chromatography (SPME-HPLC) analysis of pesticides. Crit. Rev. Anal. Chem. 2005, 35, 71–85.
6. Spietelun, A., Kloskowski, A., Chrzanowski, W., Namiesnik, J., Understanding solid-phase microextraction: Key factors influencing the extraction process and trends in improving the technique. Chem. Rev. 2013, 113, 1667–1685.
7. Tienpont, B., David, F., Bicchi, C., Sandra, P., High capacity headspace sorptive extraction. J. Microcol. Sep. 2000, 12, 577–584.
8. Nerin, C., Salafranca, J., Aznar, M., Batlle, R., Critical review on recent developments in solventless techniques for extraction of analytes. Anal. Bioanal. Chem. 2009, 393, 809–833.
9. Lan, H., Rönkkö, T., Parshintsev, J., Hartonen, K., Gan, N., Sakeye, M., Sarfraz, J., Riekkola, M.-L., Modified zeolitic imidazolate framework-8 as solid-phase microextraction Arrow coating for sampling of amines in wastewater and food samples followed by gas chromatography-mass spectrometry. J. Chromatogr. A 2017, 1486, 76–85.

10. Helin, A., Rönkkö, T., Parshintsev, J., Hartonen, K., Schilling, B., Läubli, T., Riekkola, M.-L., Solid phase microextraction Arrow for the sampling of volatile amines in wastewater and atmosphere. J. Chromatogr. A 2015, 1426, 56–63.
11. Lee, J. Y., Kim, W. S., Lee, Y. Y., Choi, Y. S., Choi, H. Jang, H. W., Solid-phase microextraction Arrow for the volatile organic compounds in soy sauce. J. Sep. Sci. 2019, 42, 2942–2948.
12. Zhang, X. Y., Wang, C. C., Wang, L. L., Chen, S., Xu, Y., Optimization and validation of a head space solid-phase microextraction-arrow gas chromatography-mass spectrometry method using central composite design for determination of aroma compounds in Chinese liquor (Baijiu). J. Chromatogr. A 2020, 1610, 460584.
13. Evans, D. G., Duan, X., Preparation of layered double hydroxides and their applications as additives in polymers, as precursors to magnetic materials and in biology and medicine. Chem. Commun. (Camb) 2006, 485–496.
14. Sansuk, S., Nanan, S., Srijaranai, S., New eco-friendly extraction of anionic analytes based on formation of layered double hydroxides. Green Chem. 2015, 17, 3837–3843.
15. Sajid, M., Basheer, C., Layered double hydroxides: Emerging sorbent materials for analytical extractions. Trends Anal. Chem. 2016, 75, 174–182.
16. Abdolmohammad-Zadeh, H., Rezvani, Z., Sadeghi, G. H., Zorufi, E., Layered double hydroxides: a novel nano-sorbent for solid-phase extraction. Anal. Chim. Acta, 2011, 685, 212–219.
17. Zhou, Q., Lei, M., Li, J., Zhao, K., Liu, Y., Determination of 1-naphthol and 2-naphthol from environmental waters by magnetic solid phase extraction with Fe@MgAl-layered double hydroxides nanoparticles as the adsorbents prior to high performance liquid chromatography. J. Chromatogr. A, 2016, 1441, 1–7.
18. Abolghasemi, M. M., Yousefi, V., Piryaei, M., Synthesis of carbon nanotube/layered double hydroxide nanocomposite as a novel fiber coating for the headspace solid-phase microextraction of phenols from water samples. J. Sep. Sci. 2015, 38, 1344–1350.
19. Liu, Y. L., Zhou, J. B., Zhao, R. S., Chen, X. F., Using Zn/Al layered double hydroxide as a novel solid-phase extraction adsorbent to extract polycyclic aromatic hydrocarbons at trace levels in water samples prior to the determination of gas chromatography-mass spectrometry. Anal. Bioanal. Chem. 2012, 404, 1603–1610.
20. Sajid, M., Basheer, C., Daud, M., Alsharaa, A., Evaluation of layered double hydroxide/graphene hybrid as a sorbent in membrane-protected stir-bar supported micro-solid-phase extraction for determination of organochlorine pesticides in urine samples. J. Chromatogr. A, 2017, 1489, 1–8.
21. Tang, S., Lee, H. K., Application of dissolvable layered double hydroxides as sorbent in dispersive solid-phase extraction and extraction by co-precipitation for the determination of aromatic acid anions. Anal. Chem. 2013, 85, 7426–7433.
22. Fang, Q., Chen, B., Self-assembly of graphene oxide aerogels by layered double hydroxides cross-linking and their application in water purification. J. Mater. Chem. A 2014, 2, 8941–8951.
23. Fang, L., Hou, J., Xu, C., Wang, Y., Li, J., Xiao, F., Wang, D., Enhanced removal of natural organic matters by calcined Mg/Al layered double hydroxide nanocrystalline particles: Adsorption, reusability and mechanism studies. Appl. Surf. Sci. 2018, 442, 45–53.
24. Hough, R., Archer, D., Probert, C., A comparison of sample preparation methods for extracting volatile organic compounds (VOCs) from equine faeces using HS-SPME. Metabolomics 2018, 14, 19.
25. Huang, N. H., Wang, J. Q., A new route to prepare nanocomposites based on polyvinyl chloride and MgAl layered double hydroxide intercalated with laurylether phosphate. Express Polym. Lett. 2009, 3, 595–604.
26. Moreira, N., Lopes, P., Cabral, M., Guedes de Pinho, P., HS-SPME/GC-MS methodologies for the analysis of volatile compounds in cork material. Eur. Food Res. Technol. 2016, 242, 457–466.
27. Wypych, J., Tadeusz, M., Determination of volatile organic compounds (VOCs) in water and soil using solid phase microextraction. Chem. Anal. (Warsaw) 2002, 47, 507–530.
28. Chang, X., Wang, Z., Quan, S., Xu, Y., Jiang, Z., Shao, L., Exploring the synergetic effects of graphene oxide (GO) and polyvinylpyrrodione (PVP) on poly(vinylylidenefluoride) (PVDF) ultrafiltration membrane performance. Appl. Surf. Sci. 2014, 316, 537–548.
29. Perestrelo, R., Silva, C., Silva, P., Camara, J. S., Global volatile profile of virgin olive oils flavoured by aromatic/medicinal plants. Food Chem. 2017, 227, 111–121.
30. Kopperi, M., Ruiz-Jiménez, J., Hukkinen, J. I., Riekkola, M.-L., New way to quantify multiple steroidal compounds in wastewater by comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometry. Anal. Chim. Acta. 2013, 761, 217–226.
31. Li, J., Xu, H., A novel polyaniline/polypyrrole/graphene oxide fiber for the determination of volatile organic compounds in headspace gas of lung cell lines. Talanta, 2017, 167, 623–629.
32. Figueiredo, J. L., Functionalization of porous carbons for catalytic applications. J. Mater. Chem. A. 2013, 1, 9351–9364.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: Li X, Lan H, Hartonen K, Jussila M, Wang X, Riekkola M-L. Layered double hydroxide/poly(vinylpyrrolidone) coated solid-phase microextraction Arrow for the determination of volatile organic compounds in water. *J Sep Sci*. 2020;1-9.
https://doi.org/10.1002/jssc.202000239